FULL PAPER

Salalens and Salans derived from 3-Aminopyrrolidine: Aluminium Complexation and Lactide Polymerisation

Luke Britton, Daniel Ditz, James Beament, Paul McKeown,* Helena C. Quilter, Kerry Riley, Mary F. Mahon and Matthew D. Jones*

Abstract: In this paper a series of 7 salalen ligands based on an aminopyrrolidine backbone have been prepared and characterised. Several systems have been reduced to the salan ONNO type-ligand. All ligands have been complexed to Al(III) with Al(**1-7**)Me, Al(**2a**)(O*i*Pr) and Al(**7a**)Me being characterised by single-crystal X-ray diffraction. In general the Al(III) centres are best described as being in a trigonal bipyramidal geometry. The solution and solid-state structures are discussed. All complexes have all been trialled for the production of PLA from *rac*-lactide, the salalen complexes had a preference for heterotactic PLA (P_r = 0.71), whereas the salan had a more isotactic bias (P_m = 0.72). In all cases PLA with low dispersities and predictable molecular weights were prepared. The activity of the two classes of ligands is compared with the salan complexes appearing to be significantly more active than the salalen systems.

Introduction

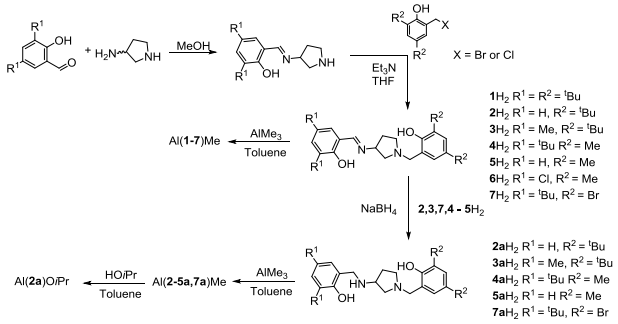
The development of biobased polymers is a key target for the 21st Century. This is mainly due to our reliance on plastic materials for all aspects of our everyday lives. One of the success stories in this arena in undoubtedly the development of polylactide (PLA) which is currently commercially produced via the controlled ring opening polymerisation (ROP) of lactide.[1] PLA has several major advantages, namely 1) it can be prepared from annually renewable starch rich materials; 2) the polymer is biodegradable under appropriate conditions; 3) PLA is biocompatible and has found many uses as tissue engineering scaffolds, resorbable sutures and stents;[2] 4) the physical properties of the resultant polymer can be tuned for a multitude of uses.[1c, 3] The physical properties (T_m, and degradation rate/profile) of PLA prepared from the racemic monomer (*rac*-LA) can be altered by the production of either atactic, heterotactic or stereoblock isotactic PLA. In this regard the choice of initiator is pivotal in determining the stereochemical outcome of the polymerisation. There have been many elegant examples in recent years based on a plethora of Lewis acid metal centres and ligand combinations.[1a, 1b, 4] However, there is still an element of serendipity in the stereochemical outcome of the polymerisation. In recent years we have published widely on the use of salalen ligands complexed to Al(III) and Zr(IV) for the controlled ROP of *rac*-LA to produce various levels of tacticity control.[5] These studies have highlighted that subtle changes in the substituents on the ligand can have dramatic changes in the stereochemical outcome of the polymerisation.[5g] Moreover, we have also shown that the activity of an Al(III)-salalen can be dramatically enhanced by simple reduction of the imine moiety.[6] Kol and co-workers have published Al(III)-O*i*Pr systems based on a chiral aminomethylpyrrolidine salalen moiety.[7] These complexes were highly selective for the production of PLA with a gradient isotactic multiblock microstructure. At 80 °C with a [LA]:[Al] ratio of 100, conversions of 42 – 91 % were achieved, depending on the substituents on the ligand, whilst the P_m (P_m = the probability of meso enchainment) values ranged from 0.23 – 0.82. Further examples of metal-salalen complexes that show significant selectivity during polymerisation include group 4 based on phenylene-salalen ligands,[5c, 8] iron-salalen based on a variety of backbones with P_m values up to 0.80;[5a] further Al(III) examples based on ethylene-salalen backbones;[9] lanthanide examples with ethylene-salalen complexes have shown a preference for the production of heterotactic PLA.[10] In this paper we have prepared a series of salalen/salan ligands based on the racemic aminopyrrolidine backbone and reacted the resultant ligands with $AlMe_3$ to generate a pre-catalyst for the ROP of *rac*-LA. A series of steric and electronic effects have been studied.

Results and Discussion

As part of our continuing studies regarding the application of salalen and salan complexes for the production of PLA a series of ligands based on 3-aminopyrrolidine were synthesised in high yield, Scheme 1. The ligands were prepared *via* a simple imine condensation followed by reaction with an alkyl halide to generate the tetradentate ONNO salalen (**1**-**7**H_2).

Mr L. Britton, Mr D. Ditz, Dr. H.C. Quilter, Miss K. Riley, Dr. M.F. Mahon Corresponding Author(s): Drs P. McKeown and M.D. Jones
Department of Chemistry
University of Bath
Bath BA2 7AY UK
E-mail: p.mckeown@bath.ac.uk and mj205@bath.ac.uk

Supporting information for this article is given *via* a link at the end of the document. Full experimental details, NMR spectra and a selection of GPCs, MALDI-ToF's, kinetic data and the X-ray data in the .cif format.



Scheme 1. Preparation of the salalen ligands **1**H_2-**7**H_2 and reduction to salan ligands **2a, 3a, 4a, 5a, 7a**H_2 and the respective complexes.

All ligands were characterised by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and high resolution mass spectrometry. **1**-**7**H_2 have a ^{1}H resonance at ca. 8.20 – 8.30 ppm ($CDCl_3$) for the imine moiety. These ligands were chosen as they impart differing steric and electronic effects upon the two fragments of the salalen system, in an attempt to discern structure-activity-relationships, e.g. **1**-**3**H_2 study the sterics of the salen fragment, **4**-**6**H_2 further interrogate the sterics/electronics of the salen fragment and **1**H_2 vs **4**H_2 and **2**H_2 vs **5**H_2 investigate the sterics of the salan moiety. The ligands were reacted with 1 equivalent of $AlMe_3$, in toluene, to generate the required complexes (Scheme 1) in low/moderate yields (10 - 56%). For Al(**2a**)Me the corresponding O*i*Pr complex was prepared for melt studies and as a comparison to our previous work utilising an analogous 6-membered ring salalen system.[6] All the salalen complexes Al(**1-7**)Me were characterised by multi nuclear NMR spectroscopy and in the solid-state by single crystal X-ray diffraction, Figure 1 and Table 1 for the metric data. The solid-state structures indicate that the aluminium centre is best described as pseudo trigonal bipyramidal with a τ value greater than 0.5 in all cases, with similar values obtained for all complexes. As expected the ligand coordinates in a tetradentate fashion, with the Al-N_{imine} bond length being significantly shorter {1.954(9) – 1.998(6)} than the Al-N_{amine} bond length {2.229(3) – 2.171(3)}. The Al-O and Al-C are also analogous to previously reported Al-salalen complexes.[7]

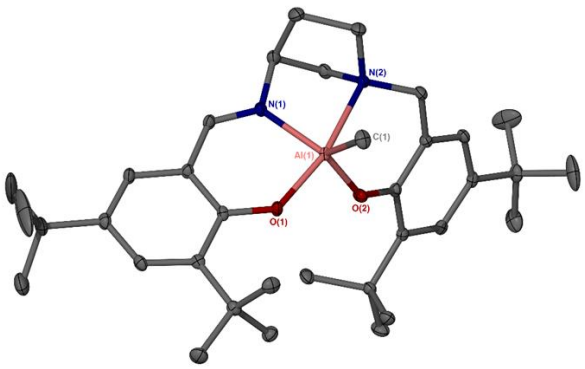


Figure 1. Representative solid-state structure for Al(**1**)Me, ellipsoids are shown at the 30% probability level and all hydrogen atoms have been removed for clarity.

The solution-state NMR spectra (see supporting information) are consistent with the solid-state structures being maintained in solution. This is exemplified by a single 3H resonance at ca. – 0.2 to – 0.5 ppm for the Al-Me moiety, and there are discrete doublets for the –CH_2– moieties indicating that the ligands are "locked" once coordinated to the aluminium centre. Upon coordination to the aluminium centre N(2) becomes chiral and with the carbon centre in ring adjacent to the imine N(1) already being chiral (albeit racemic). It is possible to observe two diastereoisomers in solution (*R,R*/*S,S* or *R,S*/*S,R* enantiomeric pairs) and it is clear that only one set of diastereoisomers is present for the isolated Al(**1**-**6**)Me. Analysis of the solid-state structures indicates this to be the *R,R*/*S,S* pair of enantiomers. The isolation of only one set of diastereoisomers may explain the low isolated yields of these complexes. However, the situation is more complicated for Al(**7**)Me where in solution two sets of diastereoisomers are observed for the isolated species.

Table 1. Selected metric data for complexes Al(**1-7**)Me, bond lengths are in (Å) and angles (°).

	Al(**1**)Me	Al(**2**)Me	Al(**3**)Me	Al(**4**)Me	Al(**5**)Me	Al(**6**)Me	Al(**7**)Me
Al(1)-O(1)	1.830(2)	1.833(2)	1.8260(15)	1.8189(13)	1.8276(18)	1.834(6)	1.804(2)
Al(1)-O(2)	1.764(2)	1.751(2)	1.7594(15)	1.7578(12)	1.7607(17)	1.754(6)	1.781(2)
Al(1)-N(1)	1.985(3)	1.982(2)	1.9878(17)	1.9823(15)	1.996(2)	1.998(6)	1.954(3)
Al(1)-N(2)	2.229(3)	2.184(2)	2.2155(17)	2.2101(15)	2.222(2)	2.197(7)	2.171(3)
Al(1)-C(1)	1.971(4)	1.983(3)	1.966(2)	1.9752(18)	1.971(3)	1.954(9)	1.962(4)
O(1)-Al(1)-N(2)	163.16(11)	164.94(9)	164.15(7)	165.62(6)	165.95(9)	166.0(3)	162.05(12)
O(2)-Al(1)-N(1)	118.23(12)	116.09(10)	115.63(7)	113.65(6)	112.85(9)	115.4(3)	118.32(15)
N(1)-Al(1)-N(2)	75.86(11)	76.91(9)	76.66(7)	76.98(6)	76.48(8)	76.8(3)	75.85(12)
τ	0.67	0.69	0.69	0.71	0.69	0.70	0.69

It has been shown previously that reduction of the imine moiety of the salalen to generate an ONNO salan ligand dramatically increases the activity of the resultant aluminium complex for the ROP of *rac*-LA.[6] Thus, in this study a selection of salalen ligands were reduced with $NaBH_4$ to generate the desired salan ligands in good yield (96 – 69 %), Scheme 1. The novel salan ligands were characterised by NMR spectroscopy, where the loss of the salalen's characteristic imine resonance and the presence of a new –CH_2– group observed, and high resolution mass spectrometry. The complexes were simply prepared in an analogous fashion to ligands **1-7**H_2. For the salan ligands only one Al-Me complex could be characterised in the solid-state {Al(**3a**)Me} by single-crystal X-ray diffraction, Figure 2. However, it was possible to prepare and isolate in the solid-state an example of an Al-O*i*Pr complex with ligand **2a**H_2, Figure 2. For these complexes the solution-state species were slightly more complicated with the generation of three chiral centres upon coordination to the Al(III) centre {N(1), N(2) and the carbon atom in the ring adjacent to N(1)}. The solution-

state NMR spectra are more complicated, in all cases there is one major Al-Me resonance and two smaller resonances (ca. 10%). DOSY spectroscopic analysis for Al(**4a**)Me indicated that these have similar diffusion constants in solution and can therefore be tentatively assigned as different stereoisomers present in solution. In the case of our previously reported salalen/salan system based on the six membered piperidine ring, a subtle difference in coordination of the salan ligand was noted in the solid-state.[6] This is not the case for Al(**2a**)O*i*Pr with N(2) and O(1) adopting the "axial" positions, as observed for the salalen systems. However, for Al(**3a**)Me compared to Al(**3**)Me there is a stark difference in the geometry of the Al(III). For the salan system, the Al(III) centre is best described as square based pyramidal with a τ value of 0.34 *cf.* 0.69 for the salalen system. This may well be related to the greater degree of flexibility associated with the salan ligand.

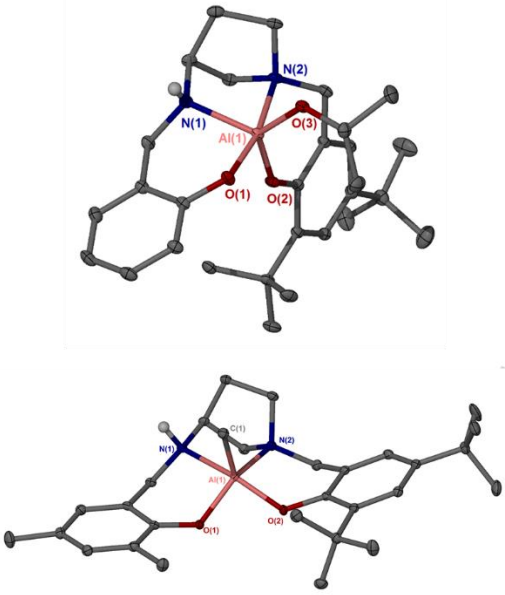


Figure 2. Solid-state structure of Al(**2a**)(O*i*Pr) (top) and Al(**3a**)Me (bottom), ellipsoids are shown at the 30% probability level. All hydrogen atoms {except those bound to N(1)} have been removed for clarity. Selected metric data {bond lengths (Å) and angles (°)}: Al(**2a**)(O*i*Pr) Al(1)-O(1) 1.7943(14), Al(1)-O(2) 1.7530(14), Al(1)-O(3) 1.7504(14), Al(1)-N(1) 2.0419(18), Al(1)-N(2) 2.1185(16), O(1)-Al(1)-N(2) 167.60(7), O(2)-Al(1)-N(1) 87.46(3), N(1)-Al(1)-N(2) 79.26(7) τ = 0.71; Al(**3a**)Me Al(1)-O(1) 1.7795(14), Al(1)-O(2) 17942(15), Al(1)-C(1) 1.982(2), Al(1)-N(1) 2.2245(18), Al(1)-N(2) 2.1194(17), O(1)-Al(1)-N(2) 135.60(7), O(2)-Al(1)-N(1) 155.88(7), N(1)-Al(1)-N(2) 76.03(6) τ = 0.34.

Initially the Al-salalen complexes were trialled for the ROP of *rac*-LA with the addition of 1 eq. of BnOH, to generate the alkoxide in-situ, at 80 °C in toluene, Table 2. At best the salalen-activity can be described as modest. To obtain conversions in excess of 50% a timeframe of 3-10 days was required. Importantly, the complexes produced PLA with controlled molecular weight and narrow dispersities. For Al(**2**)Me, PLA with a very slight isotactic bias was produced, however for the other complexes either atactic or heterotactically inclined (P_r upto 0.71) PLA was isolated. Analysis of the resultant PLA *via* MALDI-ToF mass spectrometry, revealed that the repeat unit was 144 gmol^{-1} and there was little evidence of transesterification, see supporting information. Moreover, analysis of the data clearly indicates the desired BnO– and H– end groups as expected from the classical coordination insertion mechanism. The complexes with ligands **4**,**5**,**6**H_2 were also tested under melt conditions (entries 5, 8, 11 Table 1). As expected the activity did improve with moderate conversions being achieved in hours rather than days. Comparison of the changes in sterics of the half-salen fragment (where R^2 = *t*Bu, entries 1-3) did not indicate that this was important in enhancing the activity or selectivity, as in all cases 10 days was necessary to obtain a respectable conversion. However, when R^2 was Me the sitution was different with Al(**5**)Me (R^1 = H) giving the highest conversion. The most bulky of this mini-series, Al(**4**)Me (R^1 = *t*Bu and R^2 = Me), gave a pitiful conversion after 5 days and was the worst performing under melt conditions. Comparing 2 vs 7 (R^1 = H, R^2 *t*Bu or Me) again indicated that reducing steric requirements had a positive effect on activity. Changing the half-salen substituents to a chloro moiety also appears to marginally increase the activity and selectivity (entries 9-10 vs. 7-8).

Table 2. Selected polymerisation data for the ROP of *rac*-LA with the Al(III) salalen complexes.

Entry	Init.	[LA]:[I]:[BnOH]	T °C	Time / h	Con./ %[c]	M_nTheo.[d]	M_n (GPC)[e]	Đ(GPC)[e]	P_r[f]
1	Al(**1**)Me[a]	100:1:1	80	240	74	10600	10100	1.06	0.53
2	Al(**2**)Me[a]	100:1:1	80	240	75	10800	12000	1.34	0.42
3	Al(**3**)Me[a]	100:1:1	80	240	55	7900	12100	1.10	0.42
4	Al(**4**)Me[a]	100:1:1	80	120	9	1400	-	-	-
5	Al(**4**)Me[b]	100:1:1	130	6.25	34	5000	3600	1.09	0.49
6	Al(**5**)Me[a]	100:1:1	80	24	24	3550	3400	1.08	0.59
7	Al(**5**)Me[a]	100:1:1	80	72	62	9050	5900	1.05	0.58
8	Al(**5**)Me[b]	100:1:1	130	2.5	61	8900	13600	1.30	0.68
9	Al(**6**)Me[a]	100:1:1	80	24	37	5450	10300	1.05	0.71
10	Al(**6**)Me[a]	100:1:1	80	72	72	10500	8950	1.07	0.71
11	Al(**6**)Me[b]	100:1:1	130	1.25	71	10350	20400	1.22	0.67
12	Al(**7**)Me[a]	100:1:1	80	240	19	2850	-	-	-

[a] Toluene solvent; [b] under melt conditions; [c] Determined *via* ^{1}H NMR spectroscopy; [d] Theoretical molecular weight calculated from conversion (rounded to the nearest 50): {[LA]:[I] × (Conversion × 144.13) / BnOH equiv.} + M_n (BnOH). [e] Determined from GPC (in THF) referenced against polystyrene standards. [f] P_r is the probability of heterotactic enchainment, determined *via* homonuclear decoupled ^{1}H NMR spectroscopy.

Inspired by our recent work where we observed a dramatic increase in selectivity and activity by reducing a salalen based on the six membered piperidine backbone[6] we also tested a series of salan-Al systems, Table 2. The salient comparisons are the following entries (Table 1 vs Table 2) 2 vs 1, 3 vs 5, 4 vs 6, 6 vs 9, 12 vs 11, where in all cases simply reducing the imine fragment of the salalen dramatically increases the activity. Due to the enhanced activity of these systems the pseudo first order rate constants for the polymerisation of *rac*-LA ([LA]$_0$ = 0.69 M, T = 80 °C, [LA]:[Al]:[BnOH] = 100:1:1, see

supporting information for the plots) were determined for Al(**2a, 4a, 5a**)Me as 2.9 × 10^{-3}, 2.4 × 10^{-3} and 1.1 × 10^{-3} $mins^{-1}$ respectively. Due to the very modest conversions obtained with the analogous salalen systems kinetic investigations were not attempted. For the salan series it appears that the steric bulk of the aryl substituent of the –NH– fragment is important (entry 1 vs. 4-5) with the least sterically demanding system being the most active. Complexes were trialed in the melt (Table 3 entries 3, 7, 8, 10) in these cases high conversion was achieved in a significantly shorter timeframe. Moreover, the polymerisation was controlled with narrow dispersities being observed.

In terms of selectivity only complexes based on **2-3a**H_2 showed any significant stereoselectivity with PLA possessing a moderate isotactic bias being observed. This is enhanced comparing entry 1 (Table 2) to entry 2 (Table 1) and entry 5 (Table 2) to entry 3 (Table 1). The exact nature for this changes in activity and selectivity remain unclear but maybe related to related to an –NH– interaction with the carbonyl of the in-coming/coordinated lactide or the growing polymer chain, stabilising the intermediates. However, it should be noted that the salan ligands are more flexible than the salalen and this too may affect the activity of the complexes.

Table 3. Selected polymerisation data for the ROP of *rac*-LA with the Al(III) salan complexes.

Entry	Initiator	[LA]:[I]:[BnOH]	T /°C	Time / h	Con./ %[c]	$M_{n,Theo.}$[d]	M_n $_{(GPC)}$[e]	$Đ_{(GPC)}$[e]	P_r[f]
1	Al(**2a**)Me[a]	100:1:1	80	24	83	12000	14600	1.14	0.35
2	Al(**2a**)O*i*Pr[a]	100:1:0	80	24	79	11400	24400	1.12	0.33
3	Al(**2a**)O*i*Pr[b]	300:1:0	130	2	55	23900	35000	1.18	0.36
4	Al(**3a**)Me[a]	100:1:1	80	24	42	6100	8300	1.05	0.28
5	Al(**3a**)Me[a]	100:1:1	80	48	75	10900	11600	1.12	0.30
6	Al(**4a**)Me[a]	100:1:1	80	16	95	13800	16050	1.25	0.46
7	Al(**4a**)Me[b]	100:1:1	130	0.42	95	13800	12850	1.11	0.42
8	Al(**4a**)Me[b]	300:1:1	130	0.42	61	28650	35450	1.14	0.46
9	Al(**5a**)Me[a]	100:1:1	80	6	63	9200	9700	1.31	0.56
10	Al(**5a**)Me[b]	100:1:1	130	0.33	81	11800	16650	1.30	0.55
11	Al(**7a**)Me[a]	100:1:1	80	24	94	13500	17250	1.20	0.51

[a] Toluene solvent; [b] under melt conditions; [c] Determined *via* ^{1}H NMR spectroscopy; [d] Theoretical molecular weight calculated from conversion (rounded to the nearest 50): {[LA]:[I] × (Conversion × 144.13) / alkoxides} + M_n (end groups). [e] Determined from GPC (in THF) referenced against polystyrene standards; [f] P_r is the probability of heterotactic enchainment, determined *via* homonuclear decoupled ^{1}H NMR spectroscopy.

Conclusions

A series of salalen and salan ligands and their respective Al(III) complexes have been prepared and characterised in solution and in the solid-state. All complexes {apart from Al(**3a**)Me} show a preference for trigonal pyramidal geometry. Comparison of the salalen systems appear to indicate that the steric requirements of the ligands are important in dictating activity. A strong enhancement in activity was observed for the complexes bearing the ONNO salan compared to the salalen complexes. The exact reason for this is unclear but it is postulated that the –NH- moiety plays a crucial role in stabilizing the intermediates formed during the polymerisation.

Experimental Section

The ligands were prepared via analogous procedures as previous studies,[6] full details are given in the supporting information a representative example is given in the paper below. All data were collected on a SuperNova EOS detector diffractometer using radiation CuKα (*λ*= 1.54184 Å) and all data was recorded at 150(2) K. All structures were solved by direct methods and refined on all F^2 data using the SHELXL-2014 suite of programs. All hydrogen atoms were included in idealized positions and refined using the riding model, all refinement details are given in the .cif file. All data was straightforward except for the following points; Al(**2**)Me the structure was twinned and non-merohedral twinning of 180° about the 1 0 0 (direct space) direction was accounted for (39%). Al(**5**)Me was a two component twin with the second component being generated by a 180 ° rotation around 0.44 0 -0.9 reciprocal direction (57%); Al(**6**)Me was twinned by virtue of a 180° ratio about the 0, 1, -1 reciprocal direction (48%) the structure also contained disordered toluene which was modelled with ADP restraints despite this an alert A was present in the checkcif due to disorder in one of the toluene moieties; Al(**2a**)(O*i*Pr) contains half a molecule of hexane in the asymmetric unit. CCDC numbers 1909124-1909132 contain the necessary information.

An example of a ligand and complexes preparation are given below.

2H_2: Salicylaldehyde (1.38 ml, 12.98 mmol) was added to 3,5-di-tert-butyl-2-hydroxybenzyl bromide (3.88 g, 12.98 mmol) in ethanol (50 ml) for 4 hours. The solvent was removed *in-vacuo* and the product was stirred with silica (CH_2Cl_2), filtered and solvent removed *in vacuo* (orange solid, 3.29 g, 8.05 mmol, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H, ppm); 13.03 (s, 1H), 10.90 (br s, 1H), 8.30 (s, 1H), 7.29 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 7.21 (dd, *J* = 7.9, 1.9 Hz, 2H), 6.95 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.88 – 6.82 (m, 2H), 4.02 (dq, *J* = 10.2, 4.9 Hz, 1H), 3.85 (s, 2H), 3.13 (dd, *J* = 10.3, 6.9 Hz, 1H), 2.96 – 2.86 (m, 1H), 2.87 – 2.76 (m, 1H), 2.64 (dd, *J* = 10.3, 5.3 Hz, 1H), 2.31 (dq, *J* = 13.3, 7.7 Hz, 1H), 1.97 (ddt, *J* = 12.9, 7.9, 4.7 Hz, 1H), 1.41 (s, 9H), 1.26 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ_C, ppm) 164.0 (CN), 161.0 (Ar), 154.3 (Ar), 140.6 (Ar), 135.6 (Ar), 132.5 (Ar), 131.5 (Ar), 123.03 (Ar), 123.00 (Ar), 121.6 (Ar), 118.9 (Ar), 118.7 (Ar), 117.1 (Ar), 67.6 (CH_2), 60.4 (CH_2), 59.8 (CH_2), 52.8 (CH), 35.0 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 33.6 (CH_2), 31.8 ($C(CH_3)_3$), 29.7 ($C(CH_3)_3$). Calculated m/z $[C_{26}H_{37}N_2O_2]^+$ = 409.2855, found 409.2918.

2aH_2: **2**H_2 (1.00 g, 2.45 mmol) was dissolved in MeOH (100 ml) to which $NaBH_4$ (4 eq, 0.37 g, 9.80 mmol) was added. The reaction was stirred for 12 hrs after which water (5 ml) was added. The solution was filtered and the resulting solid was re-dissolved in CH_2Cl_2 (30 ml) and washed water before being dried with $MgSO_4$ to yield a white solid (0.75 g, 1.82 mmol, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ_H, ppm); 10.75 (br s, 2H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.21 – 7.12 (m, 1H), 6.96 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.87 – 6.80 (m, 2H), 6.77 (td, *J* = 7.4, 1.2 Hz, 1H), 4.05 – 3.89 (m, 2H), 3.86 (d, *J* = 13.4 Hz, 1H), 3.73 (d, *J* = 13.4 Hz, 1H), 3.42 (q, *J* = 6.2, 4.6 Hz, 1H), 2.91 – 2.81 (m, 1H), 2.74 (t, *J* = 8.5 Hz, 1H), 2.67 (t, *J* = 5.2 Hz, 1H), 2.57 (q, *J* = 8.2 Hz, 1H), 2.26 (dtd, *J* = 13.4, 8.2, 5.2 Hz, 1H), 1.75 (dddd, *J* = 12.9, 8.2, 6.7, 4.4 Hz, 1H), 1.42 (s, 9H), 1.28 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz,

$CDCl_3$, δ_C, ppm); 158.3 (Ar), 154.1 (Ar), 140.8 (Ar), 135.6 (Ar), 129.1 (Ar), 128.5 (Ar), 123.1 (Ar), 123.0 (Ar), 122.3 (Ar), 121.4 (Ar), 119.3 (Ar), 116.7 (Ar), 59.7 (CH_2), 58.9 (CH_2), 56.3 (CH_2), 52.4 (CH), 51.0 (CH_2), 35.0 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 31.9 (CH_2), 31.8 ($C(CH_3)_3$), 29.8 ($C(CH_3)_3$). Calculated m/z $[C_{26}H_{39}N_2O_2]^+$ = 411.3006, found 411.3041.

Al(**2**)Me: **2**H_2 (0.409 g, 1.0 mmol) was dissolved in toluene (10 ml) to which $AlMe_3$ (2 M hexane, 0.50 ml, 1.0 mmol) was added. This was stirred for 4 hours after which time the solvent was removed and the solid was recrystallised from hexane/toluene mixture (pale yellow solid, 0.19 g, 0.42 mmol, 42%). ^{1}H NMR (400 MHz, C_6D_6, δ_H, ppm); 7.55 (d, *J* = 2.5 Hz, 1H), 7.19 (m, 2H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.52 (m, 1H), 4.31 (d, *J* = 13.4 Hz, 1H), 3.00 (t, *J* = 9.2 Hz, 1H), 2.72 (d, *J* = 13.4 Hz, 1H), 2.63 (m, 1H), 2.46 (d, *J* = 9.4 Hz, 1H), 1.69 (s, 9H), 1.48 (s, 1H), 1.44 (s, 9H), 1.34 (d, *J* = 9.6 Hz, 1H), 1.27 (m, 1H), 1.14 (m, 1H), -0.24 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, δ_C, ppm); 168.3 (CN),166.3 (Ar), 156.3 (Ar), 139.3 (Ar), 138.2 (Ar), 136.9 (Ar), 133.6 (Ar), 123.6 (Ar), 123.2 (Ar), 122.8 (Ar), 122.0 (Ar), 117.5 (Ar), 115.4 (Ar), 66.6 (CH_2), 57.0 (CH_2), 56.8 (CH), 50.9 (CH_2), 35.6 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 31.4 (CH_2), 29.9 ($C(CH_3)_3$). Elemental analysis ($C_{27}H_{37}AlN_2O_2$) Calcd in %: C, 72.29; H, 8.31; N, 6.24. Found: C, 72.17; H, 8.44; N, 6.19.

Al(**2a**)Me: **2a**H_2 (0.411 g, 1.0 mmol), washed with hexane (white solid, 0.22 g, 0.49 mmol, 49%). ^{1}H NMR (400 MHz, C_6D_6, δ_H, ppm); 7.52 (s, 1H), 7.22 (m, 2H), 6.84 (s, 1H), 6.68 (m, 2H), 4.02 (d, *J* = 13.4 Hz, 1H), 3.89 (t, *J* = 12.5 Hz, 1H), 2.82 (d, *J* = 14.0 Hz, 2H), 2.64 (t, *J* = 11.2 Hz, 2H), 1.91 (m, 3H), 1.59 (s, 9H), 1.42 (s, 9Hz), 1.24 (m, 1H), 1.10 (m, 1H) 1.01 (m, 1H), -0.34 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, δ_C, ppm); 162.1 (Ar), 156.2 (Ar), 139.6 (Ar), 138.4 (Ar), 130.2 (Ar), 123.8 (Ar), 123.1 (Ar), 122.6 (Ar), 121.7 (Ar), 121.3 (Ar), 120.8 (Ar), 115.5 (Ar), 58.1 (CH_2), 57.0 (CH_2), 53.8 (CH_2), 52.5 (CH), 50.4 (CH_2), 35.5 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 30.0 ($C(CH_3)_3$), 30.0 (CH_2).

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Keywords: lactide • catalyst • biopolymer • aluminium

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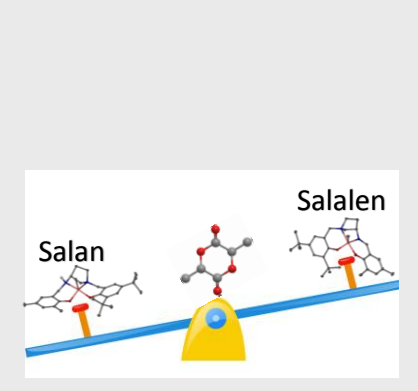
FULL PAPER

A series of Al(III) complexes with salan and salalen ligands have been prepared. These have been trialled for the controlled ROP of *rac*-LA. The salan complexes have been shown to be significantly more active for the polymerisation.



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Salalens and Salans derived from 3-Aminopyrrolidine: Aluminium Complexation and Lactide Polymerisation